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## SPECIFICATION

## METHOD AND APPARATUS FOR PRODUCING HYDROGEN

TECHNICAL FIELD

[0001]

The present invention relates to a method and apparatus for producing hydrogen by high temperature steam electrolysis. More particularly, the present invention relates to an electrolytic apparatus suitable for use in an electrolytic method that reduces the power required by electrolysis by carrying out electrolysis by feeding steam to a cathode side and reducing gas to an anode side of an electrolytic apparatus in which the electrolyzer is partitioned into the anode side and the cathode side by a solid oxide electrolyte diaphragm.

BACKGROUND ART

[0002]

Methods for the electrolysis of water for the purpose of producing hydrogen include alkaline water electrolysis, solid polymer water electrolysis, and high temperature steam electrolysis. However, because alkaline water electrolysis and solid polymer water electrolysis require an electrolysis voltage of at least 1.8 V, their electrical efficiency is no greater than 80% and they require large amounts of electrical power for hydrogen production. In contrast, high temperature steam electrolysis, which carries out the electrolysis of steam at high temperatures, about 800°C, by feeding high temperature steam to the

cathode side of an electrolyzer that has been partitioned into an anode side and cathode side using a solid oxide electrolyte as the diaphragm, can utilize thermal energy to decompose water due to the high temperatures and, in addition, can be expected to have an electrical efficiency of at least 90% due to suppression of the polarization overvoltage and resistance overvoltage. As a result, the electrolysis voltage can be dropped to no more than 1.5 V and the amount of electrical power required for hydrogen production can be reduced. An electrolytic method has very recently been introduced in which the oxygen ion that is transferred in the solid oxide electrolyte diaphragm from the cathode side to the anode side is reacted on the anode side by feeding natural gas to the anode side of the electrolyzer; through use of the chemical potential thereof for water decomposition, this electrolytic method can achieve a substantial reduction in electrical power consumption (United States Patent No. 6,051,125).

[0003]

In the method disclosed in US 6,051,125, natural gas is directly fed to the anode side of the electrolyzer and reacts with oxygen ion present on the anode side; this reaction energy assists water decomposition on the cathode side. In this case, since the depolarization action due to methane reduces the water electrolysis voltage, in principal the theoretical electrolysis voltage becomes approximately 0. While an actual water electrolytic apparatus requires a voltage that is the sum of this and

the overvoltage, US 6,051,125 claims to make possible water electrolysis at a total voltage of approximately 0.5 V.

[0004]

The electrolyzer used in conventional high temperature steam electrolysis also employs the same materials and structure as the cell of a solid oxide fuel cell (SOFC). A Ni cermet suitable for a reducing atmosphere is used as the electrode on the cathode side, where steam is introduced and hydrogen is generated, while a conductive oxide, for example, lanthanum cobaltite or lanthanum manganate, is used as the electrode on the anode side, where oxygen is generated. A conventional high temperature steam electrolytic apparatus is shown conceptually in Figure 1. In the apparatus shown in Figure 1, the electrolytic apparatus (electrolyzer) is partitioned into a cathode side and an anode side by a solid oxide electrolyte diaphragm. High temperature steam is fed to the cathode side and electrical power is supplied to the cathode and anode, and high-purity hydrogen is obtained by the resulting electrolysis of the steam on the cathode side. The oxygen ion  $O^{2-}$  generated by steam electrolysis transfers to the anode side through the solid oxide electrolyte diaphragm.

[0005]

In contrast to the preceding, both the cathode and anode are exposed to reducing gas in a process in which steam electrolysis is carried out at a reduced electrolysis power achieved through the introduction of reducing gas to the oxygen-generating anode side of the electrolyzer.

However, steam is introduced as a starting material on the cathode side, and, until hydrogen production has occurred, it is possible for the metal to undergo steam oxidation at the high temperatures involved. It is also similarly necessary to consider high temperature steam oxidation on the anode side, where steam may be introduced in order to inhibit carbon deposition and where acid gas, such as water, is produced by the electrode reactions. However, neither an electrolyzer nor process conditions adapted to these circumstances have appeared.

#### DISCLOSURE OF THE INVENTION

##### PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

An object of the present invention is to discover an electrolyzer structure that is adapted for use in a method that, as described above, produces hydrogen by steam electrolysis by feeding steam to the cathode side, feeding reducing gas to the anode side, and feeding power to the anode and cathode of an electrolyzer that is partitioned into an anode side and a cathode side by a diaphragm of solid oxide electrolyte.

##### MEANS FOR SOLVING THE PROBLEMS

[0007]

As a means of achieving this object, one embodiment of the present invention provides an apparatus that produces steam by high temperature steam electrolysis and that is provided with an electrolyzer partitioned into an anode side and a cathode side by a solid oxide electrolyte

diaphragm, a conduit that feeds reducing gas to the anode side of the electrolyzer, and a conduit that supplies steam to the cathode of the electrolyzer, wherein a cermet that comprises ceramic and metal and that is stable in a reducing atmosphere at temperatures of 400 to 1000°C is used as the material of the anode and the cathode.

[0008]

A reducing gas is fed to the anode side of the electrolytic apparatus in the present invention. As used herein, a reducing gas is a gas that can lower the oxygen concentration on the anode side in the steam electrolyzer according to the present invention by reacting with oxygen that has traversed the solid oxide electrolyte membrane to reach the anode side of the electrolyzer, and encompasses hydrocarbon gases such as natural gas and methane.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Figure 1 is a diagram that conceptually shows a conventional high temperature steam electrolytic apparatus.

Figure 2 is a diagram that conceptually shows a high temperature steam electrolytic apparatus according to the present invention.

Figure 3 is a diagram that shows an interconnector structure according to the present invention.

Figure 4 is a diagram that conceptually shows a high temperature steam electrolytic apparatus used in a second embodiment of the present invention.

Figure 5 is a flow diagram that conceptually shows one

example of a method for producing hydrogen according to the second embodiment of the present invention.

Figure 6 is a diagram that conceptually shows the hydrogen-producing apparatus used in Example 1.

Figure 7 is a diagram that shows the structure of the hydrogen-producing test apparatus used in Example 2 of the present invention.

Figure 8 is a graph that shows the results of Example 2 of the present invention.

[0010]

One embodiment of a hydrogen-producing apparatus according to the present invention is shown conceptually in Figure 2. In the hydrogen-producing apparatus according to the present invention, a reducing atmosphere is present on both the cathode side and the anode side due to the hydrogen produced on the cathode side of the electrolytic apparatus (electrolyzer) and due to the reducing gas that is fed to the anode side. Therefore, due to this exposure of both the anode and the cathode to a reducing gas, a characteristic feature of the present invention is the use of a cermet that comprises ceramic and metal and that is stable in a reducing atmosphere at temperatures of 400 to 1000°C as the material of the anode and the cathode.

[0011]

Hydrogen is produced on the cathode side of the electrolyzer by electrolysis of the introduced steam, and as a consequence the gas composition within the electrolyzer changes moving from the inlet side to the

outlet. The hydrogen concentration is lowest at the inlet and is highest at the outlet. When just steam is fed to the cathode side of the electrolyzer, metal, e.g., Ni, is subject to steam oxidation at the high temperatures involved. The admixture of a reducing gas is effective for stopping steam oxidation; however, because it is desired to produce high-purity hydrogen on the cathode side of the electrolyzer according to the present invention, the admixture of hydrogen as the reducing gas is highly suitable. Since the Ni electrodes that are in wide use in electrolyzers do not undergo steam oxidation as long as the hydrogen to steam molar ratio  $H_2/H_2O$  in the atmosphere encompassing the electrode is at least 0.01 and preferably at least 0.04, this concentration becomes the minimum required hydrogen partial pressure.

[0012]

The electrolysis voltage varies with the oxygen partial pressure on the anode and cathode sides of the electrolyzer, and making  $P_{O_2}$  (cathode side)/ $P_{O_2}$  (anode side) as large as possible is effective for lowering the electrolysis voltage.

[0013]

However, as the hydrogen concentration admixed on the cathode side of the electrolyzer is raised, the oxygen partial pressure on the cathode side declines, and, since this causes the voltage to increase, it is preferable to keep the admixed hydrogen concentration as low as possible.

[0014]

In particular, since the reducing gas/acid gas molar ratio in the vicinity of the outlet on the anode side of the electrolyzer gets to be 0.4 or less, in order to obtain a reduction in the electrolysis voltage,  $H_2/H_2O$  at the inlet on the cathode side of the electrolyzer is desirably kept at no more than 0.4 and preferably is kept at no more than 0.2.

[0015]

With regard to the admixed hydrogen, a portion of the hydrogen produced by steam hydrolysis is preferably circulated to the inlet in order to simplify the system.

[0016]

On the anode side of the electrolyzer, the reducing gas concentration is highest at the inlet and declines towards the outlet. The oxygen partial pressure is therefore lowest at the inlet and highest at the outlet. On the cathode side of the electrolyzer, on the other hand, the hydrogen concentration rises towards the outlet due to the production of hydrogen, and, accompanying this, the oxygen partial pressure declines towards the outlet. When the steam on the cathode side of the electrolyzer and the reducing gas on the anode side flow in the same direction,  $P_{O_2}$  (cathode side)/ $P_{O_2}$  (anode side) assumes a maximum value at the inlet and a minimum value at the outlet, which leads to an increase in current density nonuniformity and causes the generation of, inter alia, thermal stresses. Due to this, the steam flow on the cathode side of the electrolyzer and the reducing gas flow on the anode side



are preferably implemented as opposing flows (countercurrent).

[0017]

Carbon deposition can be inhibited by the addition of steam to the reducing gas fed to the anode side of the electrolyzer. In this case, the water to reducing gas molar ratio is desirably no more than 0.4 and preferably is no more than 0.2.

[0018]

The anode and cathode must be capable of diffusing gas, must be electronically conductive, and must have an electrocatalyst activity.

[0019]

The anode and cathode are each preferably composed mainly of a metal that does not form an oxide under conditions of  $H_2/H_2O < 0.4$ , which is a preferred atmosphere within the electrolyzer described in the preceding. Ni, Fe, Co, Cu, Pt, Ag, Pd, and Ru and their mixtures and alloys are examples of electronically conductive, catalytically active metals that do not form oxides under such conditions.

[0020]

In order to inhibit sintering at the high temperatures involved, the electrode material generally takes the form of a cermet as obtained by mixing with a ceramic powder. The admixed ceramic can be selected based on it being stable under conditions of  $H_2/H_2O < 0.4$  and based on considerations of a reactivity · bondability · thermal expansion ratio similar to that of the electrolyte material

and considering the oxygen ion conductivity or oxygen ion electronic conductivities.

[0021]

In the apparatus according to the present invention, the anode and cathode material is preferably material having an elevated oxygen ion conductivity and/or electronic conductivity as obtained by partial element substitution in, for example,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{LaCrO}_3$ ,  $\text{LaTiO}_3$ , or  $\text{LaGaO}_3$ . When, in particular, the material used exhibits both electronic and oxygen ion conductivities, this is effective for reducing the reaction overvoltage since many reaction sites will be present in the case of application as an electrode and the area available for oxygen ion diffusion is also increased.

[0022]

In addition, when a steam electrolyzer is provided with a multistage configuration by serially connecting a plurality of electrolytic cells, it becomes necessary to have an interconnector that connects anode to cathode. This interconnector is in contact with both the gas on the anode side and the gas on the cathode side of the electrolyzer, and also has the task of separating them (gas seal). In a conventional SOFC cell or high temperature steam electrolyzer cell, one side has a reducing atmosphere and the other side has an oxidizing atmosphere, a circumstance that has made it difficult to select a material suitable for these atmospheres and that has also made cell fabrication quite problematic. In specific terms,

the current situation is that only a limited number of ceramics, such as lanthanum chromite, have been found for application as interconnector materials suitable for both a reducing atmosphere and an oxidizing atmosphere, and the fabrication of fine, dense structures from these materials has been quite problematic. It has therefore been difficult to obtain a reliable gas seal at the electrode joints with interconnectors fabricated of these materials.

[0023]

In the instant process, a reducing atmosphere is present on both the anode side and the cathode side of the electrolyzer, and as a consequence metal can be used for the interconnector material. This facilitates forming and joining and enables the fabrication of an electrolytic apparatus that is robust to stress and highly reliable. Ni, Ni-based alloys, Fe-based alloys, Co-based alloys, Cu-based alloys, and Ag-based alloys are examples of interconnector materials that can be used by the present invention.

[0024]

The structure of an interconnector according to the present invention is shown conceptually in Figure 3. The electrolyzer 5 is partitioned into an outer anode side 12 and an inner cathode side 11 by a cylindrical membrane 3 of solid oxide electrolyte, and an anode 4 is disposed on the outer side of the solid oxide electrolyte and a cathode 2 is disposed on the inner side. In the apparatus shown in Figure 3, two (upper and lower) cylindrical electrode solid oxide electrolyte composites are joined across an

insulator 21, and the anode and cathode are connected in series by an interconnector 22. This makes it possible, by connecting the anodes and cathodes to a direct-current source, to maintain the voltage required for electrolysis at low current and to have the electrolysis reactions proceed. High temperature steam is fed to the cathode side 11 of the electrolyzer, a reducing gas (shown as  $\text{CH}_4$ ) is fed to the anode side 12, and electrical power is fed to both electrodes, resulting on the cathode side in the occurrence of steam electrolysis and the production of hydrogen. The generated oxygen ion transfers to the anode side through the solid oxide electrolyte. On the anode side, the reducing gas reacts with the transferred oxygen ion, producing  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . A metal as described above can be used for the interconnector in the apparatus according to the present invention because both the anode side and cathode side of the electrolyzer in the apparatus according to the present invention have a reducing atmosphere.

[0025]

The present inventors have in the past carried out research on technology that was approximately the same as in US 6,051,125 and found the following shortcoming in the method described in US 6,051,125 in which only natural gas is fed to the anode side of the electrolyzer. Data about the same as the conditions provided in US 6,051,125 were obtained when operation of the electrolyzer was first begun; however, when the operation was continued, the current value gradually declined and before long the

operation could not be continued. As a result of inquiries into the reasons for this, it was determined that when methane is directly fed to the anode side of the electrolyzer, the methane undergoes decomposition on the high temperature anode side and a film of the carbon decomposition product coats the electrode, thereby clogging the electrode.

[0026]

An object of a second embodiment of the present invention is to provide a technology that, through a simple procedure that is not too costly, can stop the problem of electrode clogging that arises due the carbon produced as described above.

[0027]

As a result of intensive and extensive investigations directed to finding a means that would achieve the aforementioned object, the present inventors discovered that the deposition of solid carbon on the electrode surface can be prevented by admixing steam or carbon dioxide into the natural gas (hydrocarbon-containing gas) fed to the anode side of the electrolyzer because the carbon produced by decomposition of the hydrocarbon-containing gas at the anode side then immediately reacts with the steam and carbon dioxide with conversion to CO or CO<sub>2</sub>. It is also possible in a high temperature steam electrolytic apparatus that utilizes a solid oxide electrolyte diaphragm to oxidize the carbon with the oxygen ion that has traveled through the solid oxide electrolyte

diaphragm to the anode side of the electrolytic apparatus. However, since the quantity of reducing gas is much larger than the quantity of oxygen ion, the deposition of solid carbon cannot be stopped just by this reaction. Moreover, the CO and hydrogen produced by the reaction between carbon and steam or carbon dioxide, being reducing gases, react with the oxygen ion on the anode side and thereby contribute to reducing the electrolysis voltage of the electrolytic apparatus.

[0028]

In addition, with respect to a high temperature steam electrolytic method for reducing electrolysis voltage by feeding steam to a cathode side and feeding hydrocarbon-containing gas to an anode side for reaction with oxygen ion, the cathode side and the anode side being provided in a high temperature steam electrolytic apparatus in which an electrolyzer is partitioned into the anode side and the cathode side using a solid oxide electrolyte as the diaphragm, the present inventors focused on the fact that the offgas discharged from the anode side of the electrolytic apparatus contains steam and carbon dioxide produced by reaction between the hydrocarbon and so forth in the feed gas and oxygen that has traversed the solid oxide electrolyte diaphragm from the cathode side. As a result, the present inventors discovered that steam and/or carbon dioxide can be conveniently admixed by admixing this anode side offgas into the hydrocarbon-containing gas that is fed to the anode side of the electrolytic apparatus.

[0029]

In other words, a second embodiment of the present invention relates to a method of producing hydrogen by high temperature steam electrolysis in which steam is fed to the cathode side of a high temperature steam electrolytic apparatus comprising an electrolyzer partitioned into an anode side and a cathode side using a solid oxide electrolyte as the diaphragm and in which the electrolysis voltage is reduced by feeding hydrocarbon-containing gas to the anode side and reacting it with oxygen ion, wherein offgas discharged from the anode side of the electrolytic apparatus is admixed into the hydrocarbon-containing gas that is fed to the anode side of the electrolytic apparatus.

[0030]

The second embodiment of the present invention also relates to an apparatus for executing the method described above. Accordingly, an additional embodiment of the present invention relates to an apparatus for producing hydrogen that is provided with an electrolyzer partitioned into an anode side and a cathode side by a diaphragm of solid oxide electrolyte, a conduit that feeds hydrocarbon-containing gas to the anode side of the electrolyzer, and a conduit that feeds steam to the cathode of the electrolyzer, wherein the apparatus is additionally characteristically provided with a conduit that admixes offgas discharged from the anode side of the electrolyzer into the hydrocarbon-containing gas that is fed to the anode side of the electrolyzer.

[0031]

Hydrocarbon-containing gas is fed to the anode side of the electrolytic apparatus in the method according to the present invention. Here, hydrocarbon-containing gas denotes natural gas or a gas that contains a hydrocarbon such as, for example, methane. The "reducing gas" expression used in this Description denotes a gas that can lower the oxygen concentration on the anode side in the steam electrolyzer according to the present invention by reacting with oxygen that has traversed the solid oxide electrolyte membrane to reach the anode side of the electrolyzer.

[0032]

The basic principal of the apparatus for producing hydrogen used in the second embodiment of the present invention, which is an apparatus that produces hydrogen by high temperature steam electrolysis using a solid oxide electrolyte membrane, is described with reference to Figure 4.

[0033]

A high temperature steam electrolyzer 113 is partitioned by a solid oxide electrolyte diaphragm 114 into an anode side 115 and a cathode side 116. High temperature steam 119 is fed to the cathode side 116 of the electrolyzer while a hydrocarbon-containing gas 110 is fed to the anode side 115 of the electrolyzer, and the high temperature steam 119 that has been fed to the cathode side 116 is electrolytically decomposed into hydrogen and oxygen



when electrical power 117 is converted to direct current by an AC-DC converter 118 and then fed to the electrolyzer. The produced hydrogen 120 is recovered as high-purity hydrogen. The produced oxygen 121, on the other hand, becomes the oxygen ion and selectively passes through the solid oxide electrolyte diaphragm 114 and is thereby transferred to the anode side 115. When, in the case under consideration, a hydrocarbon-containing gas 110 is fed to the anode side 115, the oxygen ion 121 is consumed by reaction with the hydrocarbon-containing gas. Because this contributes to setting up a concentration gradient for the oxygen ion, the voltage required for water electrolysis is reduced and a substantial decline in power consumption is achieved.

[0034]

The second embodiment of the present invention is characterized by the admixture of offgas discharged from the anode side of the high temperature steam electrolyzer into the hydrocarbon-containing gas that is fed to the anode side of the electrolyzer. This method according to the present invention is described with reference to Figure 5. The description that follows employs methane as a suitable example of the hydrocarbon gas, but the invention is not limited to this description and other hydrocarbon gases can also be used.

[0035]

In the system shown in Figure 5, the electrolysis of high temperature steam is carried out by feeding a

hydrocarbon-containing gas to the anode side of the high temperature steam electrolyzer described above, feeding high temperature steam to the cathode side of the electrolyzer, and applying power. High temperature offgas is produced on the anode side of the electrolyzer and a high temperature hydrogen-containing gas (containing hydrogen and steam) is produced on the cathode side. In the system according to the present invention, high temperature offgas discharged from the anode side of the electrolyzer is admixed into the hydrocarbon-containing gas that is fed to the anode side of the electrolyzer.

[0036]

As described in the preceding, the method according to the second embodiment of the present invention is characterized in that feed to the anode side of the electrolyzer is carried out by admixing offgas discharged from the anode side of the electrolyzer into the hydrocarbon-containing gas that is fed to the anode side of the electrolyzer. As a consequence, the steam and carbon dioxide present in the admixed offgas immediately react with the carbon produced by pyrolysis of hydrocarbon, e.g., methane, on the anode side of the electrolyzer, yielding CO or CO<sub>2</sub>. This stops the appearance of solid carbon on the anode side of the electrolyzer and prevents electrode contamination by carbon.

[0037]

However, even in this case, when the addition of steam is deficient, poisoning still occurs due to the formation

of a carbon film on the electrode. When, in order to prevent the production of a carbon film, the total addition of steam or carbon dioxide is brought to an amount equimolar with the amount of carbon (number of moles as the carbon atom) in the hydrocarbon-containing gas fed to the anode side of the electrolyzer, from a theoretical perspective carbon deposition will then be inhibited since this is an amount at which the carbon in the hydrocarbon-containing gas is all converted to CO. However, in order to more reliably prevent carbon deposition, the total addition of steam or carbon dioxide admixed into the hydrocarbon-containing gas is preferably an amount at least equimolar with the amount of carbon (number of moles as the carbon atom) in the hydrocarbon-containing gas fed to the anode side of the electrolyzer. When steam is added in excess over equimolar with the amount of carbon in the hydrocarbon, the methane carbon is oxidized as far as carbon dioxide and up to 2-fold hydrogen on a molar basis is generated accompanying the production of carbon dioxide. Since this hydrogen, as a reducing gas, reacts with the oxygen ion, almost no energy is wasted. The  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$  reaction is an exothermic reaction and it is not necessary to supply energy in order for this reaction to proceed. The  $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$  reaction (total reaction between methane and water) and the  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$  reaction are mildly endothermic reactions, and, while heat must therefore be supplied in order for the reaction as a whole to proceed, this thermal energy is

smaller than the electrical energy that is added as overvoltage during electrolysis and external heating is therefore not required.

[0038]

The energy required in order to add steam at 2-fold (molar basis) with respect to methane is fairly large, which would make it necessary in order to restrain energy consumption to utilize, through the use of a high efficiency heat exchanger, the heat of the high temperature offgas discharged from the electrolyzer. On the other hand, with regard to the components in the offgas, the water and carbon dioxide produced by methane oxidation are present at 2 : 1 and uncombusted reducing gas component (hydrocarbon such as methane) is also present. Accordingly, when offgas discharged from the anode side of the electrolyzer is, in accordance with the method according to the present invention, added to the hydrocarbon-containing gas feed rather than adding steam from the outside, heat exchange is rendered unnecessary by the direct use of this high temperature offgas; the steam and carbon dioxide present in the offgas also both function to inhibit carbon deposition, and, in addition, a more effective energy utilization can be had since the uncombusted reducing gas component has, along with the methane, a depolarization action.

[0039]

The mixed gas of methane with steam and carbon dioxide readily reacts in the presence of a catalyst at the temperatures (about 650 to 1000°C) used in high temperature

steam electrolysis according to the present invention to yield CO and hydrogen or CO<sub>2</sub> and hydrogen. By actively utilizing this reaction, the methane will all be converted to CO, CO<sub>2</sub>, and H<sub>2</sub> prior to contact with the electrode, and as a result methane decomposition and electrode contamination will not occur. Accordingly, a preferred embodiment of the present invention relates to the above-described method that is further characterized in that the mixed gas of hydrocarbon-containing gas being fed to the anode side of the electrolytic apparatus and anode side offgas, is converted, prior to contact with the anode of the electrolytic apparatus, by a thermal reaction to a mixed gas whose main components are hydrogen and carbon monoxide and is thereafter brought into contact with the anode. When, in order to realize this, a structure is elaborated in which the mixed gas of methane with steam and carbon dioxide being fed to the electrolyzer is passed through a catalyst layer prior to coming into contact with the electrode, the methane will then not come into direct contact with the electrode and the goal of preventing electrode contamination will be achieved. That is, in a more preferred structure of the electrolytic apparatus according to the present invention, a catalyst layer is disposed in the conduit that supplies the anode side of the electrolyzer with the mixed gas of hydrocarbon-containing gas and offgas from the anode side of the electrolyzer and the mixed gas of hydrocarbon-containing gas and anode side offgas is converted, prior to contact with the anode of the

electrolytic apparatus, by a thermal reaction into a mixed gas whose main components are hydrogen and carbon monoxide. [0040]

There may be insufficient energy at an overvoltage of around 0.5 V since, as described above, the production of hydrogen by the reaction between methane and water is moderately endothermic and high temperatures of 650 to 1000°C must be maintained in the high temperature steam electrolytic apparatus according to the present invention. Particularly when, for example, the overvoltage is brought down to small values through the use of a thin film of YSZ (yttrium-stabilized zirconia) for the solid oxide electrolyte diaphragm, the introduction of energy becomes necessary in order to maintain the temperature required for the steam electrolysis reactions. Since compensation with electrical energy is not a profitable strategy, the use of the energy of methane combustion is preferred. In this case, a simple method with the highest thermal efficiency comprises utilization of the heat of reaction provided by carrying out the partial oxidation reaction of methane by adding oxygen to the methane and feeding this to the electrolytic apparatus. Since the amount of oxygen required for this reaction is not very large, there is almost no hazard associated with this oxygen admixture. In addition, even when air is used rather than oxygen, the increase in waste heat due to the nitrogen is not very large. Furthermore, this reaction is made even more advantageous by the fact that the steam and CO produced by

it are useful for preventing carbon deposition on the electrode.

[0041]

Accordingly, an additional embodiment of the present invention relates to the method of producing hydrogen as described hereinabove, further characterized by mixing oxygen or air into the offgas from the anode side of the electrolytic apparatus, admixing the resulting mixed gas into the hydrocarbon-containing gas being fed to the anode side of the electrolytic apparatus, and converting the result, by the heat provided by the partial oxidation reaction of the hydrocarbon-containing gas, into a mixed gas whose main components are hydrogen and carbon monoxide.

#### Example 1

A test of hydrogen production by high temperature steam electrolysis was carried out using the test apparatus 1 shown in Figure 6. A cylinder of scandium-stabilized zirconia (SSZ), closed at one end, was used as the solid oxide electrolyte diaphragm 3, and Ni-zirconia cermet electrodes were placed on both sides thereof as the anode 2 and cathode 4. This was placed within an electrolyzer 5, thereby partitioning the electrolyzer 5 into an anode side 12 and a cathode side 11. A discharge conduit 6 was set up on the cathode side 11 to discharge the product mixed gas of hydrogen and steam. A gas inlet 7 was formed in the anode side 12 of the electrolyzer for the introduction of reducing gas (shown as  $\text{CH}_4$ ).

[0042]

High temperature steam electrolysis was carried out at 700°C by feeding methane to the anode side 12 of the electrolytic apparatus through the gas inlet 7, feeding steam through the cathode side inlet 8, and supplying power from a direct-current power source 13 to the anode 2 and the cathode 4. The production of hydrogen from the outlet 9 of the product gas discharge conduit 6 was confirmed.

#### Example 2

A test of hydrogen production by high temperature steam electrolysis according to the second embodiment of the present invention was carried out using the high temperature steam electrolytic apparatus shown in Figure 7. In the high temperature steam electrolytic apparatus 1 shown in Figure 7, electrodes (anode 2 and cathode 4) are mounted on both sides of a cylindrical solid oxide electrolyte diaphragm 3 that is closed at one end and the electrolyzer 5 is partitioned into an anode side 12 and a cathode side 11. A discharge conduit 6 is placed on the cathode side 11 to discharge the product mixed gas of hydrogen and steam. A gas inlet 7 is formed in the anode side 12 of the electrolyzer for the introduction of hydrocarbon-containing gas. This structure is about the same as that of the cell of a solid oxide fuel cell (SOFC), and the procedure for fabricating it is also almost unchanged from that for an SOFC cell. In the example under consideration, a thin film (film thickness = 100  $\mu\text{m}$ ) of YSZ (yttrium-stabilized zirconia) was used as the solid oxide electrode diaphragm 3, and electrodes 2 and 4, in each case



of a nickel cermet, were mounted on the two sides of the YSZ film 3. The outside electrode 2 was the anode and the inside electrode 4 was the cathode.

[0043]

To carry out the electrolysis test, the electrolyzer 5 was placed in an electric furnace and direct-current voltage 13 was applied to both electrodes while maintaining the temperature at 1,000°C. For the method according to the present invention, which was carried out at ambient pressure, only steam was introduced to the cathode side 11 of the electrolyzer, while a mixed gas obtained by mixing a model offgas at 2-fold as the gas volume ratio with methane was introduced on the anode side 12. The supplied model offgas was a mixture of steam, carbon dioxide, and methane in proportions of 4 : 2 : 1. An actual anode side offgas does not contain methane as an uncombusted gas, but rather contains the hydrogen and CO produced by the reaction of methane; in the present case, however, methane was substituted for the hydrogen and CO. The proportion of methane admixture was determined assuming a combustion utilization rate of about 85%. The anode side was placed on the outer side of the electrolyzer because this facilitated observation of the status of carbon deposition on the anode.

[0044]

For the comparative tests, a test was carried out according to the method of US 6,051,125, wherein, operating at ambient pressure, only steam was introduced on the

cathode side 11 and only methane was introduced on the anode side 12. Another comparative test was run in which the anode side 12 was opened up and methane was not introduced, that is, using the conditions in a conventional high temperature steam electrolytic method. In the tests, direct-current voltage was applied to the electrodes and voltage-versus-current was observed; the status of the anode was also investigated after electrolysis had been carried out for a suitable period of time.

[0045]

In the conventional steam electrolytic method, in which methane is not fed to the anode side 12, the open circuit electrolysis voltage, that is, the voltage at which current started to flow when the voltage was being raised, was approximately 0.9 V, while an electrolysis voltage of 2 V was required at  $1 \text{ A/cm}^2$ , which is a practical current value for steam electrolysis. In contrast, in the method according to US 6,051,125 and the method according to the present invention, the open circuit voltage did not assume a clear value and electrolysis current began to flow at very low voltage values; moreover, the current value rose in an approximately linear fashion as the voltage was raised and the electrolysis voltage was 1.3 V at the practical current value of  $1 \text{ A/cm}^2$ . This value is fairly higher than the numerical value estimated from the qualitatively described material in the Specification of US 6,051,125; however, this value is thought to be appropriate considering that the YSZ membrane in the electrolyzer used

in this example was thick at 100  $\mu\text{m}$ . However, when compared with high temperature steam electrolysis without the use of natural gas, the electrolysis voltage obtained in this example is still a fairly low electrolysis voltage, indicating that the theory of the US patent is in principle correct.

[0046]

The ability to prevent electrode contamination by admixing steam and carbon dioxide into the hydrocarbon-containing gas fed to the anode side of the electrolyzer was investigated by following the decline in the current value when an electrolysis voltage of 1.3 V was continued for an extended period of time. The graph given in Figure 8 shows the change in the electrolysis current value for the case of only methane feed to the anode side 12 of the electrolyzer and for the case of feed to the anode side 12 of the electrolyzer of a mixture of the model offgas at 2-fold as the volume ratio with methane. As shown in this graph, the current value underwent a continuous decline when only methane was supplied, while the current value remained approximately unchanged at its original value when the mixture of methane and model anode side offgas was supplied. With regard to the visual inspection of the electrodes (anode), a fairly substantial deposition of carbon was observed on the anode after 1 hour in the case of feed of only methane to the anode side 12 of the electrolyzer, while a clean surface was maintained even after 10 hours in the case of feed of a mixture of methane

and model offgas to the anode side 12 of the electrolyzer.

[0047]

With respect to high temperature steam electrolysis in which a hydrocarbon-containing gas (methane) is fed to the anode side of the electrolyzer, the preceding test results show that continuous operation will be quite difficult using the method of feeding only methane to the anode side of the electrolyzer since electrode clogging began to appear with this method upon electrolysis for just a few hours. However, it was shown that, when anode side offgas containing steam and carbon dioxide was added to the methane and the resulting mixture was fed to the anode side of the electrolyzer, long-term operation at a practical level became possible, almost entirely without the appearance of effects due to carbon deposition, when the amount of offgas admixed was about twice the amount of methane as the volume ratio. When separate tests were carried out in which the ratio of the steam and carbon dioxide admixed into the methane fed to the anode side 12 of the electrolyzer was varied, it was found that electrode clogging did not appear rapidly even when the amount of admixed steam was less than or equal to twice the amount of methane as the volume ratio. However, when the ratio between the methane and the total of the steam and carbon dioxide in the offgas was the equimolar ratio, the start of clogging was observed in a relatively short time. In tests to date, there has been absolutely no observation of carbon deposition when the total of the steam and carbon dioxide

added to the methane has been twice that of the methane as the molar ratio, and for this reason it is thought that the mixture of anode side offgas containing twice the steam and carbon dioxide as the molar ratio is the most preferable quantity for preventing electrode clogging. The mixture of offgas in excess of this, even if preferred with regard to electrode clogging, cannot be said to be preferred because the electrolysis current value is substantially not achieved due to the resulting decline in the concentration of the methane fed to the anode side of the electrolyzer.

[0048]

While it is possible to stop anode clogging by mixing steam from an external source in place of the anode side offgas, energy is required to produce steam from water and get up to the operating temperature (about 650 to 1000°C) of the electrolyzer, which results in excessive energy consumption when the electrolysis overvoltage is small. Moreover, because the uncombusted gas (residual methane) present in the anode side offgas is re-used in the method according to the present invention, uncombusted gas can be reduced by about 40% when compared with the admixture of steam at twice the methane on a molar basis.

[0049]

Various embodiments of the present invention are provided hereinbelow.

[0050]

1. A method of producing hydrogen by high temperature steam electrolysis for reducing electrolysis voltage by

feeding steam to a cathode side and feeding hydrocarbon-containing gas to an anode side for reaction with oxygen ion, the cathode side and the anode side being provided in a high temperature steam electrolytic apparatus in which an electrolyzer is partitioned into the anode side and the cathode side using a solid oxide electrolyte as the diaphragm, wherein offgas discharged from the anode side of the electrolytic apparatus is admixed into the hydrocarbon-containing gas that is fed to the anode side of the electrolytic apparatus.

[0051]

2. The method of producing hydrogen according to 1 above, wherein the offgas from the anode side is admixed so that the sum of the steam and carbon dioxide stands in at least an equimolar ratio with respect to the number of moles as carbon of the hydrocarbon-containing gas fed to the anode side of the electrolytic apparatus.

[0052]

3. The method of producing hydrogen according to 1 above, wherein the offgas from the anode side is admixed so that the sum of the steam and carbon dioxide is approximately twice as the molar ratio the number of moles as carbon of the hydrocarbon-containing gas fed to the anode side of the electrolytic apparatus.

[0053]

4. The method of producing hydrogen according to any of 1 to 3 above, wherein the mixed gas of anode side offgas and the hydrocarbon-containing gas that is fed to the anode

side of the electrolytic apparatus is, prior to coming into contact with the anode of the electrolytic apparatus, converted by a thermal reaction to a mixed gas whose main components are hydrogen and carbon monoxide and is thereafter brought into contact with the anode.

[0054]

5. The method of producing hydrogen according to any of 1 to 4 above, wherein oxygen or air is mixed into the anode side offgas from the electrolytic apparatus, the resulting mixed gas is admixed into the hydrocarbon-containing gas fed to the anode side of the electrolytic apparatus, and conversion is carried out, by the assist of the oxidation reaction heat of the hydrocarbon-containing gas, into a mixed gas whose main components are hydrogen and carbon monoxide.

[0055]

6. An apparatus for producing hydrogen, that is provided with an electrolyzer partitioned by a solid oxide electrolyte diaphragm into an anode side and a cathode side, a conduit that feeds a hydrocarbon-containing gas to the anode side of the electrolyzer, and a conduit that feeds steam to the cathode of the electrolyzer, and that is additionally provided with a conduit that admixes offgas discharged from the anode side of the electrolyzer into the hydrocarbon-containing gas fed to the anode side of the electrolyzer.

[0056]

7. The apparatus for producing hydrogen according to 6

above, configured in such a manner that a catalyst layer is disposed in the conduit that feeds the mixed gas of hydrocarbon-containing gas and anode side offgas from the electrolyzer to the anode side of the electrolyzer and the mixed gas of hydrocarbon-containing gas and anode side offgas is converted, prior to its contact with the anode of the electrolytic apparatus, by a thermal reaction into a mixed gas whose main components are hydrogen and carbon monoxide.

[0057]

8. An apparatus for producing hydrogen by high temperature steam electrolysis, that is provided with an electrolyzer partitioned by a solid oxide electrolyte diaphragm into an anode side and a cathode side, a conduit that feeds reducing gas to the anode side of the electrolyzer, and a conduit that feeds steam to the cathode of the electrolyzer, wherein the apparatus uses a cermet that comprises ceramic and metal and that is stable in a reducing atmosphere at temperatures of 400 to 1000°C as the material of the anode and the cathode.

[0058]

9. The apparatus according to 8 above, wherein the cermet used as the electrode material is a cermet whose main constituent is metal that does not form oxide in an equilibrium reaction at temperatures of 400 to 1000°C in an atmosphere in which the molar ratio  $H_2/H_2O$  of hydrogen to steam in the atmosphere or the molar ratio of reducing gas in the atmosphere to water is less than or equal to 0.4.



[0059]

10. The apparatus according to 8 above, wherein Ni cermet is used as the cermet used as the electrode material.

[0060]

11. The apparatus according to any of 8 to 10 above, wherein the metal cermet used as the electrode material is a material in which the main constituent of the ceramic mixed with the metal is an oxygen ion conductor or an oxygen ion · electronic conductor.

[0061]

12. The apparatus according to any of 8 to 10 above, wherein scandium-stabilized zirconia (SSZ) or yttrium-stabilized zirconia (YSZ) is used as the solid oxide electrolyte.

[0062]

13. The apparatus according to any of 8 to 12 above, that is additionally provided with a conduit that admixes a portion of the hydrogen gas produced on the cathode side of the electrolyzer into the steam fed to the cathode side of the electrolyzer.

[0063]

14. The apparatus according to any of 8 to 13 above, structured in such a manner that the flow of steam on the cathode side of the electrolyzer and the flow of reducing gas on the anode side of the electrolyzer are in countercurrent to one another.

[0064]

15. The apparatus according to any of 8 to 14 above,

wherein a plurality of anodes and cathodes are connected in series by a metal interconnector.

[0065]

16. A method of producing hydrogen by steam electrolysis in which reducing gas is fed to the anode side of an electrolyzer partitioned by a solid oxide electrolyte diaphragm into an anode side and cathode side, steam is fed to the cathode side of the electrolyzer, and power is fed to the anode and cathode of the electrolyzer, wherein hydrogen is admixed into the steam fed to the cathode side of the electrolyzer.

[0066]

17. The method according to 16 above, wherein the hydrogen is admixed into the steam fed to the cathode side of the electrolyzer in an amount that provides a molar ratio  $H_2/H_2O$  of hydrogen to steam of no more than 0.4 but at least 0.01.

[0067]

18. The method according to 16 or 17 above, wherein the flow of steam on the cathode side of the electrolyzer and the flow of reducing gas on the anode side of the electrolyzer are in countercurrent to one another.

#### INDUSTRIAL APPLICABILITY

[0068]

According to the present invention, the present invention relates to a method and apparatus for producing hydrogen by high temperature steam electrolysis and more particularly, provides an electrolytic apparatus adapted

for use in an electrolytic method that reduces the power required by electrolysis by carrying out electrolysis by feeding steam to the cathode side and reducing gas to the anode side of an electrolytic apparatus in which the electrolyzer is partitioned into an anode side and a cathode side by a solid oxide electrolyte diaphragm. The present invention also provides an optimal operating method for this electrolytic apparatus.

[0069]

With respect to the method of producing hydrogen by steam electrolysis carried out by feeding a hydrocarbon-containing gas to the anode side of an electrolytic apparatus comprising an electrolyzer partitioned into an anode side and a cathode side by a solid oxide electrolyte diaphragm and feeding high temperature steam to the cathode side of this electrolytic apparatus, hydrogen can be efficiently produced in accordance with a second embodiment of the present invention by stopping electrode clogging due to solid carbon deposition rising from pyrolysis of the hydrocarbon and by effectively utilizing the heat held by the anode side offgas post-reaction and effectively utilizing the uncombusted gas component present therein.